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Investigating the Stability of Ru-promoted Fe-based Fischer-Tropsch Catalyst at high Synthesis Gas Conversion

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Abstract

The productivity of an iron-based Fischer Tropsch (FT) process strongly depends on the synthesis gas conversion. However, iron is known to oxidize significantly at high CO conversion due to the high reactor water partial pressures. In commercial iron-based FT plant this necessitate operation at low single pass conversion, resulting in high separation and recycling cost of the tail gas and the overall economics of the process. Ruthenium has been reported to demonstrate significant stability in the presence of water, hence the employment of FT catalyst promoted with Ru is expected to permit high CO conversion. In this study the stability of an industrial Fe-based FT catalyst impregnated with ruthenium is investigated. The reactions were carried out at industrially relevant conditions in a 1 dm^3 slurry reactor at 250 °C and 20 bar. It was noted that the Fe promoted with Ru was more stable at high CO conversion implying a significant resistance to deactivation in the presence of water. An increase in CO_2 and CH_4 selectivity and a fall in C_{5+} selectivity were also noted.

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Keywords: Fischer-Tropsch; CO conversion; Synthesis gas;Iron-based FT catalyst; Ruthenium; Single pass; Tail gas; Slurry Reactor.

1. Introduction

Energy security, affordability and sustainability is a topical issue worldwide [1]. The Fischer Tropsch Synthesis (FTS) is used to produce synthetic fuels and high-value petrochemical feedstock from a mixture of hydrogen (H_2) and carbon monoxide (CO). The process provides an alternative route for the production of clean fuels from coal, natural gas, biomass and other carbonaceous materials. FT process is attracting renewed interest due to the product

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characteristics of the fuel produced with low sulphur and negligible aromatics contents [2] which can be directly substituted for or blended with conventional crude derived fuels.

The FTS employs transition metals as catalyst to convert synthesis gas (the H_2 and CO mixture) to a complex spectrum of products mainly hydrocarbons with water as a major byproduct [3, 4]. One of the main areas of improvement in FT process economics is by improving catalyst properties such as stability, selectivity and activity. Even though the transition metals Ru, Co, Fe and Ni are all active for the FTS reaction, only Fe and Co are employed commercially due to cost considerations [5, 6]. Iron catalysts are active at more severe conditions of pressure and space velocities [7] but the productivity of strongly depends on the CO conversion level [8]. On iron-based catalysts despite the significant water gas shift (WGS) reaction occurring together with the FTS, high per pass synthesis gas conversions will cause high reactor water partial pressures and result in rapid deactivation of the catalyst. This is due to the fact that iron is known to oxidise significantly during FTS at high reactor water partial pressures [8]. This renders iron-based catalyst an unattractive option for such operations.

Ruthenium (Ru) is the most active of the transition metals for FTS but mainly due to its very high price compared to iron or cobalt, it was abandoned as commercial catalyst [6, 9]. The metal however, has demonstrated significant resistance to oxidation by either water or oxygen during FTS [10]. It has been reported that high reactor water partial pressure increases the FT reactions rates on ruthenium as well as increases the chain length of the products [11] from the polymerization reactions. These have led to the claims that high synthesis gas conversions should be feasible on Ru at industrial relevant conditions thereby eliminating the need for tail gas recycling required at the current low conversion process. Studies on Fe-Ru systems have been conducted, in general, Ru was found to improve reducibility and increased conversion was observed with an increase in metals loading. The conclusion was that the catalysts were more stable due to the presence of Ru.

A single pass high synthesis gas conversion over the catalyst that eliminates the separation and recycling of the reactor tail gas in a once-through commercial FT operation will results in an improved overall economics of the FT process. The feasibility of such a process depends on the catalyst stability at such high synthesis gas conversion levels. This study investigates the industrial feasibility of a FT process conduct at a high single pass conversion of the syngas over Fe-based catalyst promoted with Ru. The emphasis is on the stability and activity of the catalyst in the prevailing high water partial pressure in the reactor.

2. Experimental

2.1 Catalyst preparation and Characterization

The 100 Fe /30 Al_2O_3/5 K_2O precursor was prepared by the method of co-precipitation of the respective nitrate salts with a precipitating agent and incipient wetness impregnation of potassium. Details of the catalyst formulation and preparation steps are reported elsewhere [12]. The calcined K-promoted catalyst was further impregnated with Ru by dissolving the required amount of the sparingly soluble organometallic complex $Ru_3(CO)_{12}$ (Sigma Aldrich, 99%) to achieve a Fe/Ru of 20 in n-hexane and added to the catalyst in a 1 L flask. The flask is sealed and allowed to stand while the change in the colour of the solution was monitored. After 3 days the colour had stabilized to a pale yellow (compared to bright yellow of the fresh solution). The slurry was transferred into a vacuum bowl and the n-hexane slowly evaporated under variable pressure at 110 ^oC. Since $Ru_3(CO)_{12}$ thermally decomposes to the base metal in an inert atmosphere at 175 °C [13], a calcination step was not deemed necessary. The organometallic complex would be reduced to its metallic state well before the FT activation temperature of 270 °C is reached.

Nitrogen chemisorption using the BET method was done using Micromeritics Tristar II 3020 to determine the morphological properties of the catalyst. The catalyst bulk phases were studied with X-ray diffraction (XRD) using a Bruker D8 Advance diffractometer with a cobalt source ($\lambda_{K\alpha1}$ = 1.78897 Å). A scanning range of 10° - 130° a scanning rate of 1 degree per minute was used with a step size of 0.01°. SEM-EDS was carried out on a FEI Nova NanoSEM 230 with an Oxford X-Max silicon drift EDS detector. The TPR profiles were obtained using a Micromeritics AutoChem 2950 to investigate the reducibility of the metal oxides under the reaction conditions. The Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) method was used to confirm the composition of the catalyst as prepared as well as confirm the elemental analysis obtained using SEM-EDS.

2.2 FTS Reaction

The catalysts were tested at 250 °C and 20 bar in a 1 dm^3 stirred, slurry reactor (stirring rate: 300 rpm). The schematic diagram of the experimental setup is shown in Figure 1.

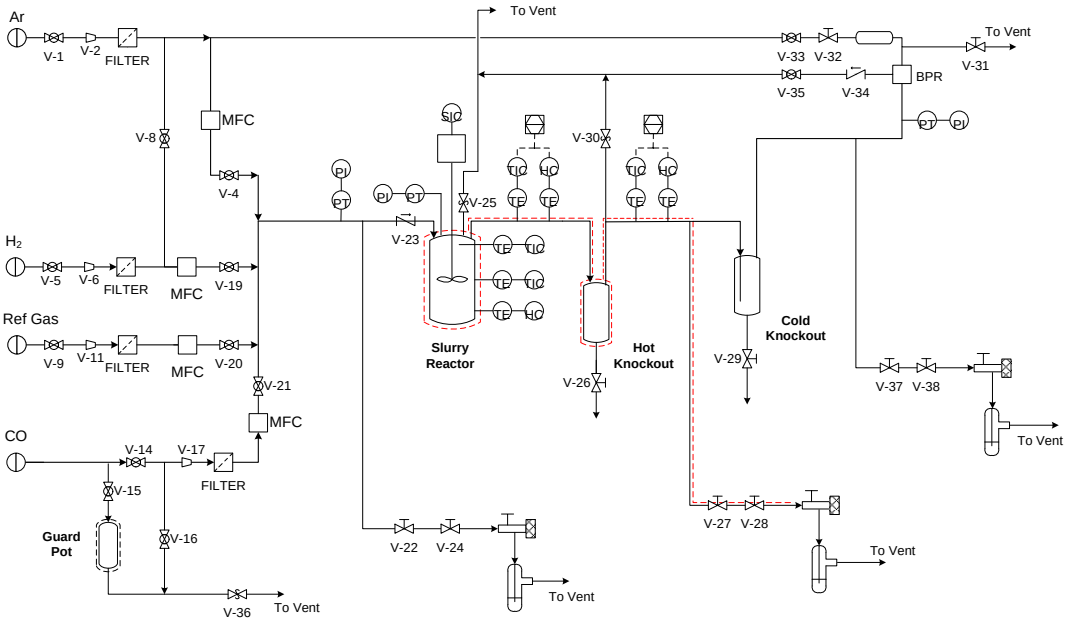

Fig. 1. Schematics of the Slurry Reactor Setup with ampoule sampling points

The reactor is initially filled with ca. 300 g of FT hard wax (Sasol, 99.9%). The wax is melted at 120 °C. 5 g of the calcined catalyst is added and the reactor is sealed under constant argon flow. The catalyst is activated *in situ* for 16 hrs at 270 °C and 1 bar using synthesis gas with a composition of H_2/CO of 2 and a GHSV of 150 mL(NTP)/g/min. After 16 hrs the reactor is purged with argon and the temperature lowered to 250 °C. The reactor is first pressurized to 20 bar with Ar and synthesis gas consisting H_2/CO/Ar = 2:1:1 at a GHSV of 200 mL(NTP)/g/min flow let in. A CO guard bed at 230 °C is used to decompose any carbonyls that may have formed in the lines. The hot knockout (at 210 °C) removes waxes from the product stream, while the cold knockout removes the liquid fraction at ambient temperature. The hot and cold knockout is drained every 24 hrs. After completing a reaction run, the system is purged with Ar and cooled to ambient pressure. The reactor temperature is lowered to 120 °C and the wax in the reactor pot removed while still liquid (the catalyst particles settle out) using a modified ladle.

2.3 Products Sampling and Analyses

The setup is fitted with an online GC-TCD to study the catalyst activity, CO_2 and CH_4 selectivity; and an ampoule sampling point for offline GC-FID analysis to carry out full products analyses. Nitrogen is used as internal standard for the GC-FID analysis. The system is initially allowed to run for 72 hrs to reach steady-state, after which ampoules are used for sampling every 24 hrs after changing the GHSV. Online GC-TCD measurements are taken at regular intervals. After taking ampoule samples of the product stream the GHSV is varied (to vary the conversion) and later returned to the initial value. The selectivities is defined by equations 1 to 4. Overall methane selectivity and CO_2 selectivity is defined as follows:

$$S_{CH_4} = Y_{CH_4}/X_{CO} \quad (1)$$

$$S_{CO_2} = Y_{CO_2}/X_{CO} \quad (2)$$

Methane selectivity and C_{5+} selectivity on the basis of volatile organic compounds (VOC) is defined as follows:

$$S'_{CH_4} = Y_{CH_4}/X_{\mathrm{CO+CO_2}} \quad (3)$$

$$S_{C_{5+}} = 1 - S'_{CH_4} - S'_{C_2} - S'_{C_3} - S'_{C_4} \quad (4)$$

3. Results and discussion

The XRD patterns of the catalysts presented in Figure 2 seem to correspond fairly closely to that of six line ferrihydrite (6LFh) with four or five of the broad peaks observed in the XRD profiles closely matching.

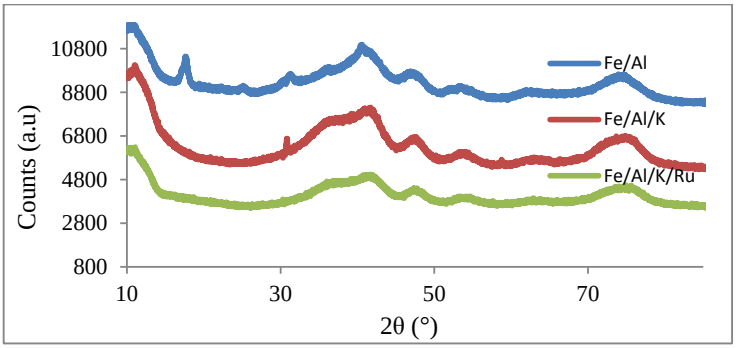

Fig. 2. XRD profiles for the catalysts

BET surface areas were calculated as 177 m^2/g, 172 m^2/g and 166 m^2/g for Fe/Al/K, Fe/Al/K/Ru and Fe/Al/K/RuCl, respectively. BJH adsorption cumulative pore volumes, in the same order, were 0.28 cm^3/g, 0.25 cm^3/g and 0.24 cm^3/g, repectively. Normalised SEM-EDS and ICP-OES results compared to the targeted elemental composition for the catalysts is shown in Table 1 (metals content only).

Table 1. Normalised elemental composition of the catalysts in wt %

Catalyst	ICP-OES				SEM-EDS				Target			
	Fe	Al	K	Ru	Fe	Al	K	Ru	Fe	Al	K	Ru
Fe/Al/K	57.24	8.45	2.53	-	57.02	9.5	2.6	-	48.83	7.75	2.44	-
Fe/Al/K/Ru	59.70	8.76	2.3	1.72	49.91	6.86	1.60	1.40	38.78	6.42	2.02	1.95

The TPR profiles of the Fe/Al/K and Fe/Al/K/Ru catalysts are shown in Figure 3. The effect of Ru in Fe/Al/K/Ru as reduction promoter is clearly evident and as expected with increased reducibility of the catalyst as compared to Fe/Al/K, similar to the results of Berry *et al.* [14] and van der Kraan *et al.* [15]. The peaks clearly shift to the left by about 100 °C.

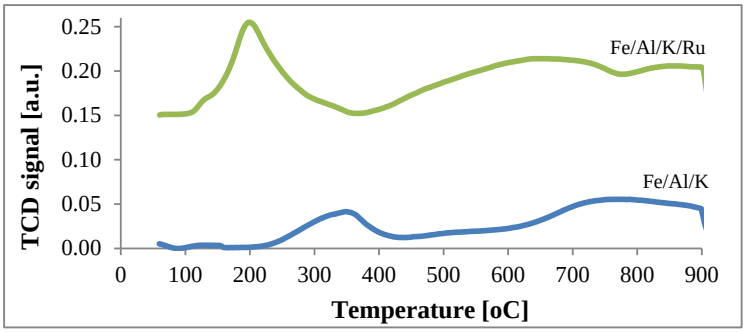

Fig. 3. TPR profiles for Fe/Al/K, Fe/Al/K/RuCl ad Fe/Al/K

A plot of CO conversion, CO_2 and CH_4 selectivity at different GHSV and with time for Fe/Al/K and Fe/Al/K/Ru catalysts are presented in Figure 4 and Figure 5 respectively. Both plots show an increasing CO-conversion with decreasing GHSV (that is, increased residence time) as expected. An initial steady-state CO-conversion of about 54% was attained at GHSV of 200 ml(NTP)/g/min and a conversion of 39 % was recorded after returning to the initial conditions. This points to an apparent deactivation of about 15 % over the roughly 410 hrs TOS. Overall CO_2 selectivity seems to rise gradually and level off, while a relatively stable overall CH_4 selectivity was observed. Decreasing space velocity and increasing conversion is known to increase CH_4 selectivity [4].

It is noted that much higher CO_2 and CH_4 selectivities are observed for Fe/Al/K/Ru. The higher methane selectivity can be linked to the enhanced activity of Ru for CO hydrogenation. This may be partly explained by Ru enhancing carburization similarly as proposed for Cu by Chonco et al [16]. A lower initial steady-state conversion was achieved for Fe/Al/K/Ru at 44% compared to Fe/Al/K at 56 %. Upon returning to initial flow conditions a steady-state conversion of around about 35 % is obtained. This implies an apparent deactivation of about 9 % over the 470 hrs TOS. In terms of stability, this is better than the 15 % deactivation observed with Fe/Al/K over 410 hrs. However, taking into account the CO_2 selectivity, this may mostly be due to less exposure to water since the catalyst seems to possess more water-gas-shift activity than its non Ru-containing catalyst.

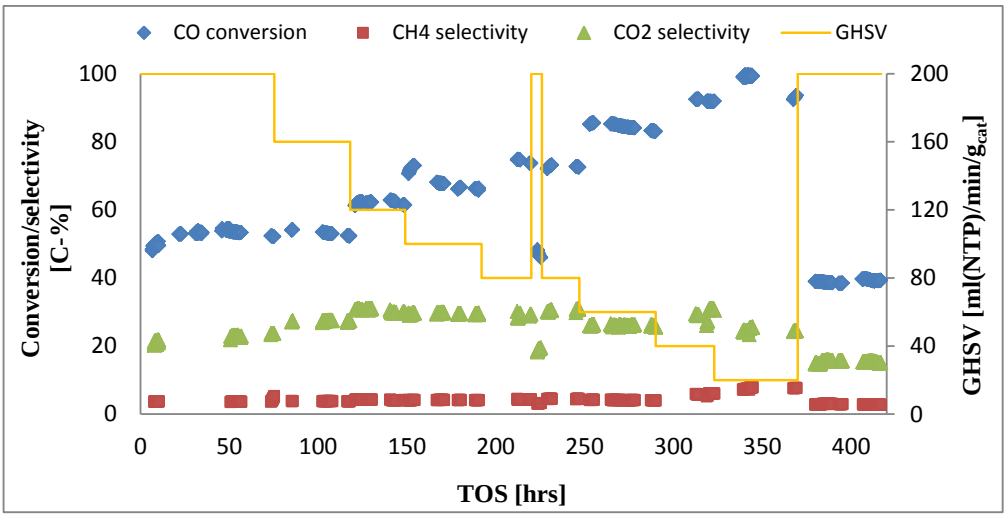

Fig. 4. CO-conversion, Overall CO_2- and CH_4 selectivity at various GHSV vs. TOS for Fe/Al/K

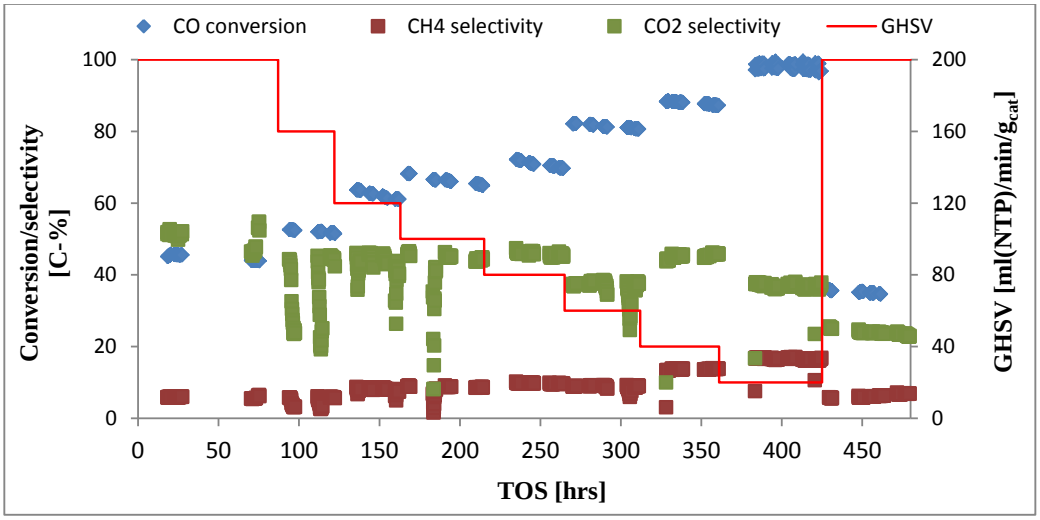

Fig. 5. CO-conversion, Overall CO_2- and CH_4 selectivity at various GHSV vs. TOS for Fe/Al/K/Ru

4. Conclusions

It could be seen that Ru promotion at 3 wt % show higher stability when comparing the apparent deactivation at high CO conversion expected due to the high water partial pressure. However, a higher CO_2, CH_4 and lower C_{5+} selectivity is obtained with Ru promotion. Since these are factors of importance when considering cost, it would seem infeasible to promote precipitated Fe-based catalysts with 3 – 5% Ru for use in LTFT at 250 °C and 20 bar. The advantages may be more apparent if used under process conditions where a lower temperature and higher pressure is utilized (closer to the optimum for Ru systems) since it has been reported that Ru performs well at temperatures of around 180 °C (or even below) and pressures at- or exceeding 100 bar [17].

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